Defect Induced Photoluminescence from Dark Excitonic States in Individual Single-Walled Carbon Nanotubes

Hayk Harutyunyan[1],* Tobias Gokus[2], Alexander A. Green[3],
Mark C. Hersam[3], Maria Allegrini[1], and Achim Hartschuh[2]
[1] *Dipartimento di Fisica "E. Fermi", Universitá di Pisa and CNISM, Largo Pontecorvo 3, 56127 Pisa, Italy*
[2] *Department Chemie und Biochemie and CeNS, Ludwig-Maximilians-Universität München, 81377 München, Germany*
[3] *Department of Materials Science and Engineering, Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3108, USA*
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We show that new low-energy photoluminescence (PL) bands can be created in semiconducting single-walled carbon nanotubes by intense pulsed excitation. The new bands are attributed to PL from different nominally dark excitons that are "brightened" due to defect-induced mixing of states with different parity and/or spin. Time-resolved PL studies on single nanotubes reveal a significant reduction of the bright exciton lifetime upon brightening of the dark excitons. The lowest energy dark state has longer lifetimes and is not in thermal equilibrium with the bright state.

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Owing to their exceptional electronic properties single-walled carbon nanotubes (SWNTs) are promising candidates for future nanoelectronic and biosensing applications as well as narrow band nanoscale emitting and detecting devices [1, 2, 3, 4]. Excitons are identified to dominate the absorption and PL emission properties of these 1–dimensional systems [5, 6]. Enhanced electron–electron interactions due to the reduced dimensionality lead to exceptionally large binding energies of the excitons that are shown to exist even in metallic SWNTs [7]. Theory predicts a manifold of excitonic bands below the free electron–hole continuum of semiconducting SWNTs [8, 9, 10, 11]. Besides the optically active odd parity singlet excitons additional even parity dipole–forbidden singlet as well as triplet excitons are expected to occur. Most importantly, some of these bands form non–emissive states that are lower in energy than the lowest bright state. This complex sequence of excitonic states and the non–radiative relaxation channels associated with them presumably have an important impact on the low PL quantum yield of SWNTs and fast exciton decay rates [12, 13, 14].

The direct experimental proof for the existence of dark excitonic states in SWNTs was presented applying two–photon photoluminescence excitation spectroscopy [5, 6] and measurements of magnetic brightening of the SWNT PL [15]. Low-energy forbidden states were also used to explain the dynamics observed in pump–probe experiments [16, 17] and the temperature dependence of PL intensities [18]. In addition, recent results on ensemble [19] and individual nanotube samples [20] have shown low energy satellite peaks in the PL spectra. These peaks were attributed to emission from low lying dark excitonic states while the mechanisms enabling optically forbidden transitions and the interplay between bright and dark excited states remain to be clarified.

In this Letter, we report on the creation of low-energy emission bands in the PL spectra of individual $(5, 4)$ and $(6, 4)$ SWNTs upon high power pulsed laser irradiation at room temperature. The persistence of these bands in subsequent low power measurements indicates that irreversible distortions of the nanotube structure efficiently "brighten" forbidden states via disorder induced mixing of excitonic states in agreement with theoretical predictions [9, 21]. The clear distinction between additional emissive features belonging to a certain nanotube and PL bands from other nanotubes is made possible by observing single nanotube spectra before and after high power irradiation and by recording the polarization dependence of bright and dark emission bands. While the decay times of the allowed transition are in the range of 1 to 40 ps [22], far longer dark state lifetimes of up to 177 ps have been observed. Based on the spectroscopic properties of the lowest dark state emission and its observation upon nanotube exposure to gold that is predicted to create high local spin densities [23, 24], we suggest that low energy emission results from triplet exciton recombination facilitated by magnetic defects and impurities.

Time-correlated single-photon counting (TCSPC) is used in combination with confocal microscopy to perform single SWNT spectroscopy and time–resolved PL measurements [22]. Spatially isolated individual SWNTs were obtained by spin-coating a small volume of micelle-encapsulated CoMoCat material onto a glass coverslip [25]. Laser excitation was provided by a Ti:Saphire oscillator operated at a photon energy of 1.63 eV and a repetition rate of 76 MHz. The PL spectra were recorded with a CCD camera and a fast avalanche photodiode was used to acquire PL transients.

Fig. 1 shows the generation of low energy satellite PL bands for two individual nanotubes. Initial spectra (solid black lines) acquired at low excitation intensity ($I_0 = 3 \cdot 10^{13}\text{photons} \cdot \text{pulse}^{-1}\text{cm}^{-2}$) show a single emission peak centered at 1.41 eV (a) and 1.46 eV (b)

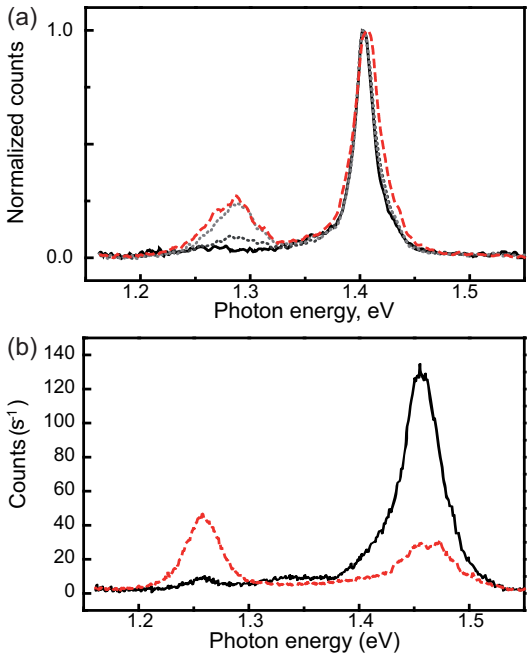

FIG. 1: Creation of low energy satellite peaks in the PL spectrum of a $(6,4)$ SWNT (a) and a $(5,4)$ SWNT (b). Initial spectra (solid black lines) acquired at low excitation intensity $I_0 = 3 \cdot 10^{13}$photons $\cdot$ pulse^{-1}cm^{-2} and considerably modified spectra (dashed red lines) of the same nanotubes acquired after exposure to high excitation intensity $\sim 17 \cdot I_0$. Low energy satellite contributions shifted by $\sim 30-60$ meV (DE_2) and $\sim 110-190$ meV (DE_1) with respect to the bright exciton emission are assigned to emission from optically dark states. Dotted grey lines in (a) were acquired sequentially between initial and final spectrum at intermediate intensity $\sim 7 \cdot I_0$ illustrating the step-like creation of the additional bands.

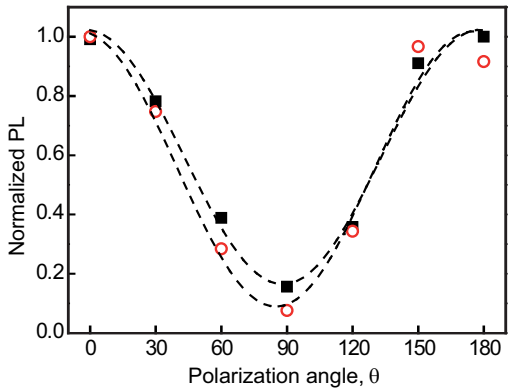

FIG. 2: Polarization dependence of the PL emission for the bright exciton BE (open circles) and the dark exciton DE_1 (filled squares) determined from a series of spectra recorded for the same (6,4) nanotube. The dashed lines are $cos^2\theta$ fits.

assigned to the allowed bright exciton (BE) in $(6,4)$ and $(5,4)$ nanotubes, respectively [26]. Irradiation of the nanotubes for 10–100 seconds with an order of magnitude higher pulse intensity $\sim 17 \cdot I_0$ results in some cases in significantly modified spectra (dashed red lines in Fig. 1) with additional redshifted shoulders and new spectral features transferring substantial spectral weight to these satellite peaks. Importantly, no such spectral changes were induced at the corresponding averaged power levels using continuous–wave (cw) excitation suggesting that high pulse intensities initiating multi-photon processes are crucial to induce these modifications. High power cw excitation, on the other hand, mainly leads to photobleaching and blinking of nanotube PL [27]. Satellite peaks for different $(6,4)$ and (5,4) nanotubes consistently appear at similar energies and can be roughly divided into two groups with redshifts of $\sim 110-190$ meV (DE_1) and $\sim 30-60$ meV (DE_2) in good agreement with Ref. [20]. The same energy splittings (130 and 40 meV) were predicted for the $(6,4)$ nanotube and attributed to triplet and even parity singlet excitons, respectively [11].

The polarization analysis of PL emission of the original BE peak and the newly created satellite DE_1 (Fig. 2) show the same $cos^2\theta$ behavior proving that the emission bands belong to the same nanotube and indicating that the redshifted emission originates from an intrinsic state of the SWNT. Furthermore, consistent appearance of the new bands in DNA wrapped SWNTs and nanotubes embedded in PMMA matrix (Fig. S1 of the supplementary information [28]) shows that the effect is not due to a chemical reaction specific to sodium cholate surfactant.

Based on these experimental observations we conclude that during the intense irradiation the structure of the nanotube is modified by creation of local defect sites. These defects alter the local symmetry of the nanotube partially removing restrictions for the population and subsequent emission from intrinsic dark states [9]. Although the spectral changes were generally irreversible, some nanotubes exhibited a reversible power dependence of the amplitude of the redshifted peak. This could indicate that some reversible structural defects are stable only at high thermal energies of the nanotube. While defects are probably ubiquitous in SWNTs, thereby explaining the observation of multiple PL peaks in the literature [19, 20, 29], their creation might be suppressed at low temperatures, where such effects were not observed under similar experimental conditions [30].

To determine the population dynamics of both dark and bright excitonic states and to study the effect of the created disorder we have performed time–resolved PL measurements of the different emission bands before and after creation of emission satellites. Fig. 3 depicts representative PL transients detected from the shaded spectral areas (shown in the insets) for two individual nanotubes of two different chiralities: (6,4) (a) and (5,4) (b). Two important conclusions can be drawn from this data. First, upon creation of the satellite peaks the bright exciton lifetime is decreased (grey curve) compared to the initial decay (black curve), and second, the DE_1 emis-

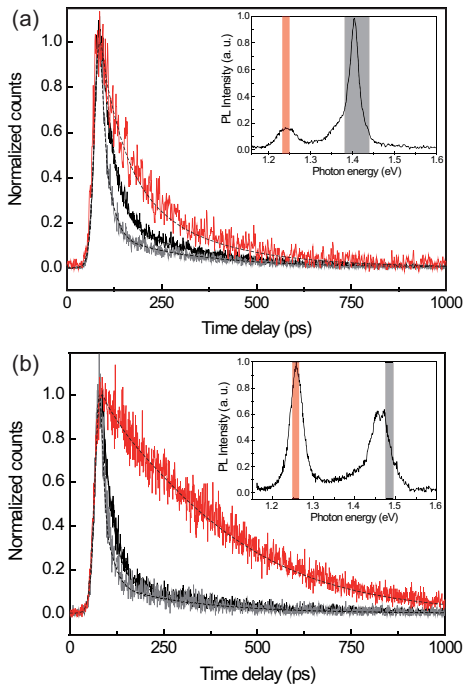

FIG. 3: PL transients visualizing the decay dynamics of different emission peaks in the spectra of individual SWNT (insets) for two different chirality nanotubes: (6,4) (a) and (5,4) (b). Black curves show the decay of the BE state detected in the grey shaded spectral range in the insets before creation of the low energy satellites. After creation of the dark state emission the decay rate of the bright exciton is increased significantly (grey lines). The decay of the dark excitonic state DE_1, shifted by 110-190 meV with respected to the BE, is substantially slower (red curves). PL decay traces detected for smaller shifts of 30-60 meV resulting from DE_2 are identical to those of the bright exciton (data not shown). Dashed lines are exponential fits to the data (see text).

sion has a much longer decay time. Monoexponential fits (dashed lines) to these transients give the lifetimes of the main emission peaks before and after creation of the redshifted band of 20 ps and 6 ps for the (6,4) nanotube Fig. 3(a) and 13 ps and 2 ps for the (5,4) tube Fig. 3(b), respectively. Importantly, the emission bands with smaller energy shifts in the range of several 10 meV (DE_2) show exactly the same decay behavior as the main peak, confirming that these states are in thermal equilibrium with the bright exciton at room temperature (data not shown) [18, 21, 31]. The decay of dark exciton DE_1 is dominated by much longer time constants, 65 ps and 177 ps for the (6,4) and the (5,4) nanotube in the present example, as would be expected for a weakly-allowed transition. Thus, other origins of the low-energy bands such as phonon replica and bi-excitons can be ruled out based on this slow decay dynamics. Additionally, we observed a fast decay component (8 ps and 2 ps) with far smaller photon flux (about factor 1/20) possibly caused by heterogeneities along the nanotube introduced by the defects or by a more complicated structure of the DE_1 excitonic manifold. Because of the large separation of the emission peaks and the detected spectral windows (shaded areas in insets in Fig. 3) overlapping emission contributions from the BE state are not sufficient to explain this decay component. On the other hand, the decay dynamics of the dark exciton is possibly complex since it involves local defects controlling both initial population and emission by making the forbidden state weakly allowed and possibly also causing non-radiative quenching. Measurements on a number of other (6,4) and (5,4) SWNTs consistently show the same effects with DE_1 lifetimes ranging up to 177 ps. Decay times derived from time–resolved PL and pump–probe data in the range of 50 - 300 ps with small relative amplitudes have been reported before [32, 33] from ensemble samples as part of multiexponential decay. We speculate that these decay times could originate from the newly created states observed here.

Now we discuss the more rapid decay of the bright exciton in the presence of the redshifted peaks (Fig. 3). Since the amplitude of the BE peak is decreased we conclude that disorder inducing defects are responsible for additional radiationless relaxation channels depopulating the bright excitonic state. Two possible competing channels can be distinguished. First, population transfer to the dark state DE_1 mediated by the introduced defects and second, decay to the ground state facilitated by enhanced exciton–phonon coupling due to defect associated local phonon modes [34]. Both relaxation channels require propagation of the bright exciton along the nanotube to enable interaction with localized defects, therefore faster decay also serves as an evidence for the mobility of excitons in nanotubes [13, 27, 35]. Population transfer from bright to dark states on the other hand would result in a delayed rise of the DE_1 emission with a rise time equal to the decay time of the bright state. Such a delayed rise, that would be detectable in our measurements especially for nanotubes with longer decay times of the BE state of up to 25 ps, was not observed suggesting that a substantial fraction of the dark state population is built up directly upon photoexcitation. Importantly, the fact that the bright exciton maintains a different and finite lifetime in the presence of the dark state DE_1 clearly shows that these two states are not in thermal equilibrium.

Based on the longer lifetimes of DE_1 state and a good agreement of its emission energy with theoretical predictions [11] we speculate that this PL band is most likely due to triplet state emission. The intersystem crossing leading to triplet emission can be assisted by coupling to high spin density states created by sidewall modification of the nanotube such as vacancy creation [36, 37]. The energy of about 5 eV needed to create a vacancy [36] can be provided through multi-photon excitation processes explaining the high pulse energies required for the creation of DE_1. In general, magnetic impurities increasing spin-orbit coupling could also be formed by trace

amounts of residual catalyst materials explaining the observation of dark state emission in other nanotube materials reported in literature. To test this possibility we treated the SWNTs with a pH neutralized, aqueous solution of gold [28] which induces spin polarized states with significant magnetic moments when adsorbed on SWNT [23] or graphene surface [24]. Covering the sample with a gold solution results in similar changes in the single nanotube PL spectrum without requiring high power pulsed excitation (Figs. S2 and S3 of the supplementary information [28]). The efficiency of brightening of the dark states is especially high when the aqueous SWNTs solution is premixed with the gold solution before deposition thus facilitating the surface adsorption of the metal. In these samples the majority of the $(6,4)$ nanotubes exhibited low energy emission sattelites, indicating that the same emissive DE_1 state is brightened. This has been further confirmed by time resolved measurements showing a broad distribution of lifetimes in the range of 7 ps to 150 ps, considerably longer than for the BE emission. Importantly, no additional PL bands have been observed in control experiments on single nanotubes deposited on gold films (not shown) as well as near-field optical experiments using sharp gold tips [38] indicating that the new PL bands are not created by metal surface induced electromagnetic field enhancement.

In conclusion, we demonstrated that nominally dark excitonic states in carbon nanotubes can become emissive after exposure to high excitation intensities and by adsorption of gold. We suggest that local defects induce mixing of different excitonic states and relaxation of selection rules via perturbation of the electronic structure. Our single nanotube measurements show that the recombination time of the excitons can be modified by the presence of disorder and that PL from the same nanotube can have decay rates varying by 2 orders of magnitude depending on the detected spectral range. While these findings are relevant for nanotube photophysics, they also indicate possible novel routes for the engineering of SWNT optical properties.

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[28] See EPAPS Document No. for supplementary information: (Fig. S1) PL spectra of a DNA-wrapped (6,4) SWNT covered by PMMA showing the creation of low energy emission sattelites upon high power irradiation. (Figs. S2 and S3) PL spectra of (6,4) SWNTs before and after exposure to gold solution.
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* Email:hayk@df.unipi.it, achim.hartschuh@cup.uni-muenchen.de